The Reaction of Benzyl Radicals with *m*-Deuteriotoluene

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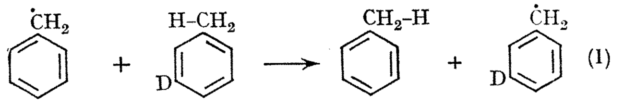
Summary Arrhenius parameters have been obtained for the title reaction in the liquid phase.

SYMMETRICAL radical transfer reactions of the type X• + Y–X → X–Y + X• are interesting from the theoretical point of view because of their simplicity. However, since the reagents and products are the same, such reactions are difficult to study, and few Arrhenius parameters are available.

We have studied the reaction



(1)

in which a *m*-deuterium is used as a label for the substrate toluene. Benzyl radicals are generated thermally from dibenzylmercury in *m*-deuteriotoluene solution at temperatures of 124—168°. This decomposition is of first order, with a rate constant given by $\log_{10}k = (14{\cdot}6 \pm 0{\cdot}2) - (36{,}200 \pm 1{,}500)/4{\cdot}576T$. The transfer reaction (1) competes with the dimerization of the benzyl (and *m*-deuteriobenzyl) radicals. From the proportions of di-, mono-, and non-deuteriated bibenzyls produced in the reaction, estimated by mass spectrometry, the rate of the transfer reaction (1) can be determined[1] if the rate constants for the decomposition of the mercurial (this work) and for the dimerization of benzyl radicals[2] are known. A value of $\log_{10}k_1$ (l.mole^{-1}sec.$^{-1}$) = $(10{\cdot}5 \pm 3{\cdot}7) - (19{,}900 \pm 2100)/4{\cdot}576T$ is obtained.

The activation energy of 19·9 kcal. mole^{-1} is significantly higher than the (gas-phase) value for the reaction of the methyl radical with methane[3] (14·7 or 14·9 kcal. mole^{-1}, probably typical for thermoneutral reactions of alkyl radicals with alkanes): this suggests that in the transition state, there is less benzylic stabilisation in the two benzyl groups than is present in the single benzyl radical in the reagents or products. On the assumption that the base of the activation energy barrier is no broader than usual for hydrogen transfer reactions, the high activation energy observed should correspond to a relatively tall, thin barrier suitable for non-classical transfer (tunnelling).[4] We have obtained deuterium isotope effects (k_H/k_D) of 6·7, 6·8 at 168·0° and 7·3, 8·0 at 155·0° for the reaction of benzyl radicals with octadeuteriotoluene (k_D), (k_H from reaction 1]. These values, after taking account of the likely magnitude of the secondary isotope effects caused by the deuterium atoms, indicate that substantial tunnelling is occurring in reaction 1. A more detailed discussion will be presented elsewhere.

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